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# Advanced Materials

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### **Editorial**

The importance of diversity in people has been known to increase performance, i.e., enhance

innovation and impact. At the same time the current geo-political climate together with societal problems has shown us that this need for diversity is essential on all fronts, to ensure our quality of life and transition towards a more sustainable future. Diversity is a strength of the Advanced Materials Research in Groningen as once again demonstrated in this magazine. Scientists from the different institutes, i.e., Zernike Institute for Advanced

Materials, Stratingh, GBB, GRIP and ENTEG, work intimately together in one organisation on materials science themes crossing borders between physics, chemistry, biology and/or engineering. This unique day-to-day cross-fertilisation and collaboration lowers the barrier to conduct out-of-thebox experiments often leading to ground-breaking discoveries.

In this edition of the magazine, we try to highlight the breadth of topics; from quantum dots, via light driven molecular motors, conductivity, (synthetic) biological cells and membranes, to bio basedelectronic wearables and implants, while taking inspiration from nature, like RNA and seal whiskers. So, our message to you: Listen to others, learn from each other, be creative and brave, and get

inspired!



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# In this Issue



### GBB

# How cells control their borders

### By Rene Fransen

Bacteria, fungi, and yeast are very good at excreting useful substances such as weak acids. One way in which they do this is through passive diffusion of molecules across the cell membrane. At the same time, cells need to prevent leakage of numerous small molecules. Yeast cells, for instance, can live in hostile environments thanks to a very robust and relatively impermeable membrane system. Biochemists at the University of Groningen have <u>studied</u> how the

composition of the membrane affects passive diffusion and the robustness of the cell membrane. Their results, which were published in Nature Communications 25 March, could help the biotech industry to optimize microbial production of useful molecules and help in drug design.



Border control is very important to cells. Their membranes separate the inner and outer environments, which are quite different. To absorb useful compounds, such as nutrients, or to excrete waste,

If you can use passive diffusion instead of an active transport system, you need fewer parts to construct such a cell.

cells can use selective transport systems. However, some transport across the membrane takes place by passive diffusion. This is a nonselective process that will let some molecules go in or out, depending on their size and hydrophobicity, for example. Active transporters have been studied extensively; however, our knowledge of passive diffusion through the membrane is still very incomplete.

### **Synthetic Vesicles**

This is a problem for the biotechnology industry, which uses cells as factories to produce a myriad of useful substances and that needs these worker cells to survive under harsh conditions. for example in an environment with a high alcohol or weak acid concentration. Bert Poolman, Professor of Biochemistry at the University of Groningen, was approached by a biotech company that was interested in producing lactic acid in bacteria. They wanted to know more about passive diffusion. This fitted in nicely with another project that Poolman is working on. 'We are highly interested in these passive transport processes because of our involvement in a project to build a synthetic cell,' says Poolman. 'If you can use passive diffusion instead of an active transport system, you need fewer parts to construct such a cell.'

So, he combined

both questions in a research project. 'We started out with a systematic study of what causes the differences in permeability of yeast membranes and bacterial membranes,' says Poolman. His team created synthetic vesicles that were made up of three to four different lipids. Ergosterol or cholesterol was added to the membranes to affect their fluidity and rigidity. A range of small molecules was tested using this system and the results from these experiments guided molecular dynamic simulations of diffusion through membranes. The in-silico studies, supervised by Professor Siewert-Jan Marrink, provided a deeper insight into the molecular mechanism of diffusion.

#### Tweaking

The fatty acid tails of the lipids turned out to be most important in determining the properties of membranes, whereas the hydrophilic head groups had little effect on the permeability. The length of the tails also mattered. 'And saturated tails, with no double carbon bonds, are stiffer than unsaturated ones. Hydrophobic interactions cause a close packing of these tails, resulting in a gel phase that is not very penetrable,' explains Poolman. Sterols increase the fluidity but in the case of yeast, which uses ergosterol, the permeability remains low. 'Thus, by tweaking the saturation of the fatty acids and the type and amount of sterol in the membrane, we can modify the permeability of the plasma membrane of yeast and bacterial cells."

Our study highlights the importance of the membrane composition of the targeted cells and this could help in drug design.

Poolman and his colleagues have, therefore, defined a number of variables that alter the permeability of membranes for different classes of compounds. This information can be used by companies that use yeasts or bacteria as cell factories. 'However, our results cannot be directly applied to those cells,' warns Poolman. 'Real membranes contain hundreds of different lipids and the composition can vary between different locations in the membrane. In addition, these cell membranes contain all kinds of proteins. If you make

changes in, for example, the lipid composition of the membrane, a lot can go wrong and the function of a membrane protein can be affected.'

### **Drug Design**

The increased understanding of the physical processes that affect permeability can help companies to understand why certain cells are better for specific processes than others. 'The usual way to tweak strains is by directed evolution. Our results will help companies to better understand the results of those optimizations and guide their cell engineering efforts.'

Another application is the design of drugs that act inside cells. 'Pharmaceutical companies use a set of empirically established rules to optimize drugs for action inside cells, based on parameters such as size or polarity. Our study highlights the importance of the membrane composition of the targeted cells and this could help in drug design.'

### Light-driven molecular motors light up

### By Rene Fransen

Rotary molecular motors were first created in 1999, in the laboratory of Ben Feringa, Professor of Organic Chemistry at the University of Groningen. These motors are driven by light. For many reasons, it would be good to be able to make these motor molecules visible. The best way to do this is to make them fluoresce. However, combining two light-mediated functions in a single molecule is quite challenging. The Feringa laboratory has now succeeded in doing just that, in two different ways. These two types of fluorescing light-driven rotary motors were described in Nature Communications (30 September) and Science Advances (4 November).



'After the successful design of molecular motors in the past decades, an important next goal was to control various functions and properties using such motors,' explains Feringa, who shared in the 2016 Nobel Prize in Chemistry. 'As these are light-powered rotary motors, it is particularly challenging to design a system that would have another function that is controlled by light energy, in addition to the rotary motion.'

### Dye

Feringa and his team were particularly interested in fluorescence since this is a prime technique that is widely used for detection, for example in biomedical imaging. Usually, two such photochemical events are incompatible in the same molecule; either the light-driven motor operates and there is no fluorescence or there is fluorescence and the motor does not operate. Feringa: 'We have now demonstrated that both functions can exist in parallel in the same molecular system, After the successful design of molecular motors in the past decades, an important next goal was to control various functions and properties using such motors.

which is rather unique.'

Ryojun Toyoda, a postdoctoral researcher in the Feringa group, who now holds a professor position at Tohoku University in Japan, added a fluorescent dye to a classic Feringa rotary motor. 'The trick was to prevent these two functionalities from blocking each other,' says Toyoda. He managed to quench the direct interactions between the dye and the motor. This was done by positioning the



Two photofunctions, Photoluminescence (PL) and unidirectional rotation, are combined by hybridizing a PL dye and a molecular motor. The molecular design provides photoregulation of these functions as well as additional synergistic effects. | Illustration Ryojun Toyoda

dye perpendicular to the upper part of the motor to which it was attached. 'This limits the interaction,' Toyoda explains.

### Applications

In this way, the fluorescence and the rotary function of the motor can coexist. Furthermore, it turned out that changing the solvent allows him to tune the system: 'By varying the solvent polarity, the balance between both functions can be changed.' This means that the motor has become sensitive to its environment, which could point the way for future applications.

### **Different Colours**

Co-author Shirin Faraji, professor of Theoretical Chemistry at the university of Groningen, helped to explain how this happens. Kiana Moghaddam, a postdoc in her group, performed extensive quantum mechanical calculations and demonstrated how the key energetics governing the photoexcited dynamics strongly depend on the solvent polarity.

Another useful property of this fluorescing motor molecule is that different dyes could be attached to it as long as they have a similar structure. 'So, it is relatively easy to create motors that are glowing in different colours', says Toyoda.

### Antenna

A second fluorescent motor was constructed by Lukas Pfeifer, also while working as a postdoctoral researcher in the Feringa group. He has since joined the École Polytechnique Fédérale in Lausanne, Switzerland: 'My solution was based on a motor molecule that I had already made, which is driven by two low-energy near-infrared photons.' Motors that are powered by near-infrared light are useful in biological systems, as this light penetrates deeper into tissue than visible light and is less harmful to the tissue than UV light.

'I added an antenna to the motor molecule that collects the energy of two infrared photons and transfers it to the motor. While working on this, we discovered that with some modifications, the antenna could also cause fluorescence,' says Pfeifer. It turned out that the molecule can have two different excited states: in one state, the energy is transferred to the motor part and drives rotation, while the other state causes the molecule to fluoresce.

### Wave Function

'In the case of this second motor, the entire molecule fluoresces,' explains Professor Maxim Pshenichnikov, who performed spectroscopic analysis of both types of fluorescent motor and who is a co-author of both papers. 'This motor is one chemical entity on which the wave function is not localized and, depending on the energy level, can have two different effects. By altering the wavelength of the light, and thus the energy that the molecule receives, you get either rotation or fluorescence.' Faraji adds: 'Our synergized in principle and in practice approach highlights the interplay between theoretical and experimental studies, and it illustrates the power of such combined efforts.'

Now that the team has combined both motion and fluorescence in the same molecule, a next step would be to show motility and detect the molecule's location simultaneously by tracing the fluorescence. Feringa: 'This is very powerful and we might apply it to show how these motors might traverse a cell membrane or move inside a cell, as fluorescence is a widely used technique to show where molecules are in cells. We could also use it to trace the movement that is induced by the light-powered motor, for instance on a nanoscale trajectory or perhaps trace motor-induced transport on the nanoscale. This is all part of follow-up research."



The dual-function motor was prepared by chemically attaching an antenna to a molecular motor. Rotation and photoluminescence (PL) can be controlled using light of different wavelengths. | Illustration Lukas Pfeifer

# Giant magnon spin wave conductance in ultrathin insulators

When you make conducting wires thinner, their electrical resistance goes up. This is Ohm's law, and it is generally right. An important exception is at very low temperatures, where the mobility of electrons increases when wires become so thin that they are effectively two-dimensional. Now, University of Groningen physicists, together with colleagues at Brest University have observed that something similar happens with the conductivity of magnons, spin waves that travel through magnetic insulators, much like a Mexican wave through a stadium. The increase in conductivity was spectacular, and occurred at ambient room temperature. This observation was published in Nature Materials on 22 September.

### Wave

Electrons have a magnetic moment, called spin, which has a value of 'up' or 'down'. It is possible to accumulate one type of spin by sending a current through a heavy metal, such as platinum (see figure). When those spins carried by electrons encounter the magnetic insulator YIG (yttrium iron garnet), the electrons can't pass through.



Magon transport in ultra-thin YIG. The current (I) through the injector electrode generates magnons in the thin YIG layer. These flow towards the detector electrode, where they produce an electrical voltage (V). | Illustration University of Groningen / Xiangyang Wei

However, at the interface with YIG, the spin excitation is passed on: magnons (who can also carry spin) are excited. These spin wave pass through the magnetic insulator like a Mexican wave in a stadium: none of the electrons (the 'spectators') move from their place, but they nevertheless pass on the spin excitation. At the detector electrode the reverse process happens: the magnons make electronic spins, which then produce an electrical voltage which can be measured. explains Bart van Wees, Professor of Applied Physics at the University of Groningen and specialist in fields such as spintronics.

Motivated by the increase of electron mobility in 2D materials, his group decided to test magnon transport in ultrathin (nanometers) YIG films. 'These films are not strictly 2D materials, but when they are thin enough, the magnons can only move in two dimensions', Van Wees explains. The measurements, performed by PhD student Xiangyang Wei, produced a surprising result: The spin conductivity went up by three orders of magnitude, in comparison to YIG bulk material.

### **Dramatic Effects**

Scientists don't use terms like 'giant' lightly, but in this case, it was fully warranted, says Van Wees, 'We made the material 100 times thinner, and the magnon conductivity went op 1,000 times. And this didn't happen at low temperatures, as is required for high electron mobility in 2D conductors, but at room temperature.' This result was unexpected and, so far, unexplained. Van Wees: 'In our paper we give a tentative theoretical explanation which is based on the transition from 3D to 2D magnon transport. But that cannot fully explain the dramatic effects we observe.'

So, what could be done with this giant magnon conduction? 'We don't understand it', says Van Wees. 'Therefore, our current claims are limited. This is enabling research that might point the way to some new yet undiscovered physics. In the long run, this might produce new devices as well.' First author Xiangyang Wei adds: 'Because there is no electron transport involved, the magnon waves produce no conventional heat dissipation. And heat production is a big problem in ever smaller electronic devices.'

### Superconductivity

And as magnons are bosons (i.e. they have integer spin quantum values), it might be possible to create a coherent state comparable to a Bose-Einstein condensate. Van Wees: 'This might even produce spin superconductivity.' All this is for the future. For now, the giant magnon conductance in YIG is well documented. 'The measurements are clear. We are looking forward to a good collaboration of theoretical physicistsprdu and experimentalists.'

## High Speed AFM reveals membrane transporter

Researchers from Groningen and Japan have recorded realtime movies of the nanoscale movements of transporter proteins. These proteins are found in the membrane of cells and have as task to specifically transport certain molecules into or out of the cell. Due to their minute size, researchers typically can only indirectly study transporter dynamics. With the recently developed High Speed-Atomic Force Microscopy (HS-AFM) it is now possible to follow in real-time the movements of these nanometer sized, naturemade machines. The results are published in Proceedings of the National Academy of Sciences USA.

shuttles citrate across the cvtoplasmic membrane of bacteria and crystal structures suggested an elevator type of transport mechanism with two states. However, up-to-date no dynamic measurements had been performed to validate or falsify this. Using HS-AFM the dynamic up-and-down movement of these tiny machines was confirmed, but unexpectedly instead of two, three states were discovered. These states only differed ~0.5 nm in height. This successful collaboration between the labs of prof. dr. Dirk Slotboom of the GBB and prof. dr. Wouter Roos of ZIAM was brought to the next level after the travels of first author dr. Sourav Maity to Japan. Here the

technical approach was perfected and the collaboration with the Japanese colleagues turned out very fruitful.

Reference: Sourav Maity, Gianluca Trinco, Pedro Buzón, Zaid R. Anshari, Noriyuki Kodera, Kien Xuan Ngo, Toshio Ando, Dirk J. Slotboom, Wouter H. Roos\* High Speed-Atomic Force Microscopy reveals a three state elevatormechanism in the citrate transporter CitS Proc. Natl. Acad. Sci. U. S. A., 2022, 119 (6), e2113927119

The studied molecular transporter

## The untapped potential of RNA structures

The human genome has just over 20,000 genes coding for proteins. Yet, it produces at least ten times that many different non-coding RNA molecules, which can often take on more than one shape. At least some of this RNA structurome is functional in physiology or pathophysiology. In an invited review for Nature Reviews Genetics, Danny Incarnato, a molecular geneticist from the University of Groningen (The Netherlands), and his colleague Robert C. Spitale from the University of Irvine in California (USA) describe ways to

develop the, as yet, largely untapped potential of RNA structures. Their paper was published on 8 November.

RNA is perhaps best known as the intermediate between genome and protein synthesis: messenger RNA molecules copy the genetic code of a gene in the cell's nucleus and transport it to the cytoplasm, where ribosomes translate the code into a protein. However, RNA is also a key regulator of almost every cellular process and the structures that are adopted by RNA molecules are thought to often be key to their functions.

### Function

Danny Incarnato, Assistant Professor of Molecular Genetics, has long been interested in the role of RNA structures in the cell and works on methods to elucidate the different structures in living cells. So, when he was invited to write a review on RNA structures, he accepted without hesitation. 'And I was happy to invite my friend and colleague Robert Spitale, one of the pioneers of the "RNA revolution", to join me.' In recent years, the knowledge of RNA molecules in the cell has increased dramatically. The ENCODE project revealed the huge number of non-coding RNAs in cells; in human cells, over ten times higher than the number of coding genes. 'Not all of them have a function,' Incarnato stresses. 'But many do, and with regard to their variety, we have barely scratched the surface.'

### **Drug Research**

Different types of non-coding RNAs have been known for a long time and it was also clear that their structure could play an important role. An example are riboswitches: RNAs that can respond to changes in the external environment by changing shape, which in turn can affect specific gene activity. 'We also knew that RNA molecules can act as enzymes,' says Incarnato. 'And, of course, ribosomes are RNA structures.' Thus, RNA molecules can act as sensors, catalysts, switches, or scaffolds and affect RNA

translation, but can also affect RNA degradation and alternative splicing.

It is, therefore, no surprise that RNAs have rapidly gained momentum in drug research. Yet, our knowledge of the 'structurome' is still very limited. 'So far, we have almost exclusively looked at single structures. But RNA molecules are very dynamic and molecules with the same sequence can take on different shapes,' explains Incarnato. 'Due to the way these structures were determined, they are often averages of all the possible conformations of a single molecule.'

### **RNA Viruses**

Incarnato has pioneered methods to uncover the structural heterogeneity of RNA molecules. 'We can combine this with high throughput RNA-sequencing to probe the structural heterogeneity.' In some cases, different structures are just an 'evolutionary by-product', while in other cases they are functional. Incarnato: 'In this way, RNA molecules can regulate practically anything inside a cell and, therefore, play a role in both physiology and pathophysiology.

Although the developments in this field are rapid, they don't proceed in a very orderly manner. Incarnato: 'There is applied pharmaceutical research going on alongside lots of fundamental research.' Interfering with RNAs could be an important way to fight diseases, including those caused by RNA viruses such as SARS-CoV2. 'Yet, we don't have a clue about off-target effects. For small molecules that interfere with specific enzymes, such as kinases, profiling panels are available to evaluate off-target profiles. However, we don't know how many RNAs have similar shapes. We really need a clear map of the RNA structurome.'

### Software

Another problem is that in many cases, it is impossible to know which of the different structural versions of a given RNA molecule is responsible for its function or dysfunction. 'And on top of that, RNAs can interact and create complicated regulatory networks. So, we also need a deeper understanding of how this works in cells.'

There is a lot of work still to do. In addition, software is important; computer programs are needed to translate biochemical analyses of RNAs into their different structures. Incarnato: 'In our field, you need to know as much about coding as about high throughput sequencing. All of us are at home both in wet labs and in bioinformatics.'

<u>Reference</u>: Robert C. Spitale & Danny Incarnato: Probing the dynamic RNA structurome and its functions. Nature Reviews Genetics, 8 November 2022 GBB

### Zernike

## Magnetoelectric crankshaft

A crankshaft converts linear motion of a piston, for example in an internal combustion engine into rotational motion of a wheel. It was known to Romans, played a crucial role in the industrial revolution and still is an essential part of many vehicles and devices. A team of researchers from the Vienna University of Technology, Istituto Italiano di Tecnologia, Beijing Institute of Technology, Rutgers University and University of Groningen found a magnetic material Gd2Mn2O5 that works similarly to crankshaft. Half of all Mn spins in this material rotate as a magnetic field applied along a fixed direction increases and subsequently decreases to zero. In contrast to the usual magnetization precession, spins in Gd2Mn2O5 only rotate when the magnetic field varies. The magnetic crankshaft works like a



Gd2Mn2O5 belongs to a family of multiferroic materials, which

magnetic moments can be controlled by applying voltage and the direction of electric dipoles can changed by an applied magnetic field. Remarkably, in one half of the 4-stroke cycle the electric polarization is nearly constant, whereas in another half its direction is reversed. This behavior can be traced back to the microscopic interaction between magnetic and electric dipoles and can be used in magnetic memory and data processing devices.

Another interesting property of this magnetic crankshaft is the unidirectional rotation of spins. To switch the rotation direction (to switch from forward to reverse gear), one has to change the orientation of the magnetic field by about 20 degrees. At first glance,

this ratchet-like motion seems to defy physical laws. During one rotation cycle, the magnetic state of the system changes 4 times in two possible sequencies: 1->2->3->4->1... and 1->4->3->2->1... and since the energies of states 2 and 4 are equal and it was initially unclear how the system in state 1 makes the choice between the two. Theoretical studies of magnetism in Gd2Mn2O5 revealed the trick: the energy barriers separating states 1 and 2, and states 1 and 4 are not the same. As the magnetic field strength varies, one of the two barriers disappears first, which is how the rotation direction is selected.

The realization of the crank mechanism in Gd2Mn2O5 is very complex. It involves two spin chains of Mn ions as well as magnetic Gd ions located between the chains. However, numerical simulations suggest that this mechanism can also work in magnets with simple

structures, showing that this unusual behavior can be found in many other materials.

Reference: Ponet, L., Artyukhin, S., Kain, T., Wettstein, J., Pimenow, A., Shuvaev, A., Wang, X., Cheong, S.W., Mostovoy, M., & Pimenov, A. Topologically protected magnetoelectric switching in a multiferroic. Nature 607, 81-85 (2022).

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# Why seal whiskers are super sensors

### By Rene Fransen

The PhD project goes back to a study published in 1998. Scientists showed that a deaf and blind seal was still able to track a swimming fish. A robot fish was used to rule out that the seal could smell its prey. Somehow, the whiskers alone are enough. The seals could even find a fish hiding behind a solid object, just from the wake leading there.

Zheng first used a laser scanner to image the whiskers of harbour seals and grey seals. This was done with the help of the Dutch Seal Rehabilitation and Research Centre Pieterburen. The whiskers were not plain cylinders, but had an undulating shape. The ratio between the 'wave length' of the undulations and the diameter appeared to be the same in the two seal species.

In a water flow, a cylinder starts to vibrate because of the turbulence that is produced behind it. Zheng observed that an undulating whisker hardly vibrated at all. He confirmed this both with flow experiments with artificial objects and with numerical simulations with real seal whiskers. He also placed a whisker behind a cylinder in a water flow system. In this experiment, the whisker did vibrate.

Zheng's conclusion is that whiskers are not vibrating under normal circumstances. He confirmed this with observations that show how, Seals can already detect the wake of a fish at 180 metres distance. PhD student Xingwen Zheng analysed whiskers from two seal species to find out how they do it. He will defend his thesis on this subject on 19 December.

at normal swimming speed, the seal whiskers do not vibrate. This means that they are sensitive to any disturbance in the water flow, like the wake of a passing fish.

Furthermore, a seal can have around 60 (grey seal) to 90 (harbor seal) whiskers, which increase in size from near the nose to near the mouth. Zheng's experiments and simulations show that such an array of whiskers increases their sensitivity as a wake detector. All in all, Zheng has shown how whiskers in two different seal species are sensitive enough to detect the wake of a passing fish at large distances.

But his thesis is not only of interest to biologists. The whiskers are real super sensors for flow detection. This could be interesting for tracking underwater life or underwater objects like submarines. Another application could be in robotic fish technology. They might use whisker-based sensors to detect where the other robot fish are and use their wake to reduce the energy required for underwater trips. In this way, they would mimic real fish, which swim more efficiently in schools.

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### A fresh look at metals reveals a 'strange' similarity

### By Rene Fransen

Our theoretical understanding of the way in which metals conduct electricity is incomplete. The current taxonomy appears to be too blurry and contains too many exceptions to be convincing. This is the conclusion that materials scientists from the University of Groningen reached after thoroughly examining the recent literature on metals. They analysed more than 30 metals and show that a simple formula can provide a classification of metals in a more systematic manner. Their analysis was published in Physical Review B on 29 August.



Metals conduct electricity, but not all in the same way. Scientists differentiate several classes of metals with names such as 'correlated', 'normal', 'strange', or 'bad'. Metals in these classes differ, for instance, in the way that their resistivity responds to increasing temperatures, 'We were interested in metals that could change from conductor to insulator and vice versa', explains Beatriz Noheda, Professor of Functional Nanomaterials at the University of Groningen. She is the scientific director at the CogniGron research centre, which develops materials-centred systems paradigms for cognitive computing. 'For this purpose, we would like to make materials that can be not just insulators or conductors, but that can also change between those states.'

### Something Unexpected

When studying the literature on metal resistivity, she and her colleagues found that the demarcation between different classes of metals was not clear-cut. 'So, we decided to have a look at a large sample of metals.' Qikai Guo - former postdoctoral researcher in Noheda's team and now at the School of Microelectronics of Shandong University, China and their colleagues from the University of Zaragoza (Spain) and CNRS (France) used the change in resistivity at increasing temperatures as a tool to compare more than 30 metals, partly based on literature data and partly based on their own measurements.

> We could fit all the data sets with the same type of formula

'The theory states that the resistivity response is dictated by the scattering of electrons and that there are different scattering mechanisms at different temperatures,' explains Noheda. For example, at very

low temperatures, a quadratic increase is found, said to be the result of electron-electron scattering. Yet, some materials ('strange' metals) show a strict linear behaviour that is not vet understood. Electron-phonon scattering was thought to take place at higher temperatures and this results in a linear increase. However, scattering cannot increase indefinitely, which means that saturation should occur at a certain temperature. Noheda: 'Yet, some metals show no saturation within the measurable temperature range and these were referred to as 'bad' metals.'

When analysing the responses of the different types of metals to increasing temperatures, Noheda and her colleagues ran into something unexpected: 'We could fit all the data sets with the same type of formula.' This turned out to be a Taylor expansion, in which the resistivity r is described as

r = r0 + A1T + A2T2 + A3T3..., inwhich T is the temperature, while r0 and the various A values are different constants. 'We found that using just a linear and a quadratic term is enough to produce a very good fit for all the metals,' explains Noheda.

Our formula is a purely mathematical description, without any physics assumptions, and depends on just two parameters.

### **More Transparent**

In the paper, it is shown that the behaviour in different types of metals is determined by the relative importance of A1 and A2 and by the magnitude of r0. Noheda: 'Our formula is a purely mathematical description, without any physics assumptions, and depends on just two parameters.' This means that the linear and quadratic regimes do not describe different mechanisms, such as electron-phonon and electron-electron scattering, they just represent the linear (through incoherent dissipation, where the phase of the electron wave is changed by the scattering) and nonlinear coherent (where the phase is unchanged) contributions to the scattering. In this way, one formula can describe the resistivity for all metals-be they normal, correlated, bad, strange, or otherwise. The advantage is that all metals can now be classified in a simple manner that is more transparent for nonexperts. But this description also brings another reward: It shows that the linear dissipation term at low temperatures (called Planckian dissipation) shows up in all metals. This universality is something that others had already hinted at, but this formula shows clearly that this is, indeed, the case.

Noheda and her colleagues are no metal specialists. 'We came from outside the field, which meant that we had a fresh look at the data. What went wrong, in our opinion, is that people looked for meaning and linked mechanisms to the linear and quadratic terms. Perhaps, some of the conclusions extracted in this manner need to be revised. It is well-known that the



Metals can be classified according to their values of r0 and  $T^* = A1/A2$ , where these coefficients follow simple trends shown in this plot.

theory in this field is incomplete.' Noheda and her colleagues hope that theoretical physicists will now find a way to re-interpret some of the previous results thanks to the formula that they found. 'But in the meantime, our purely phenomenological description does allow us to compare metals from different classes.'

<u>Reference</u>: Qikai Guo, César Magén, Marcelo J. Rozenberg, and Beatriz Noheda: Phenomenological classification of metals based on resistivity Phys Rev B, 29 August 2022 Zernike

### Wearable electronics from starch to prevent e-waste

### By Rene Fransen

Soft, wearable sensors can improve our lives, but these soft and stretchable electronic devices are nearly impossible to recycle. As a result, this electronic waste usually ends up in landfills or polluting the environment. Polymer scientists from the University of Groningen have developed a starch-based polymer that makes it possible to create a fully biodegradable soft material for sensors. They published a paper on this new material in ACS Applied Materials & Interfaces on 13 December.

Soft, stretchable polymers are used to make various kinds of electronic devices. They are used for example in smart watches to make contact with the skin. Sensors in shoes or clothing are also often based on these materials, as is the screen of your smartphone. 'These soft materials are often made from mixtures of polymers, which are difficult to purify. As a result, they are dumped in landfills, often with the toxic metal components of the sensor still present. This kind of electronic waste is becoming a serious problem', says Xiaohong Lan, first author of the paper and postdoc at the University of Groningen Polymer Science group led by Professor Katja Loos.



#### Production of ASSET | Illustration Xiaohong Lan, University of Groningen

#### **Backbone**

Lan, Loos, and their colleagues have developed an alternative to these complex polymers: a biodegradable material that decomposes in a matter of weeks to a few months. 'There are easy ways to remove the metal and polymers from the e-waste', says Lan. 'Of course, you could try to recycle the soft polymers, but that is often too complex, and therefore too expensive.' The researchers' new polymer decomposes, leaving only water and carbon dioxide behind.

'To create a biodegradable polymer, we started out with a backbone of starch-derived dextrin carbohydrates,' explains Lan. 'Most polymer backbones contain chemical bonds, which are very strong. The dextrin backbone can be degraded by natural enzymes that are present in soil.' Long fatty acid tails were added to the dextrin in the backbone, and the researchers were able to use the amount of fatty acids added per glucose unit to regulate the so there is no reason why this biodegradable ASSETm should not replace traditional soft polymers in smart electronics. Lan: 'However,



ASSET is a soft, stretchable polymer for wearable electronics | Photo Xiaohong Lan, University of Groningen

hydrophobicity of the polymer. 'The enzymes that degrade the polymer require water, so if a material is too hydrophobic, they cannot do it. If the polymer is too hydrophilic, on the other hand, the material will not have the right properties.'

### **Brushes**

The material needs to be soft and stretchable, but also dielectric, which means that the sensors can charge themselves with the electricity created by rubbing against fabric. Apart from the fatty acid tail, the modified dextrin polymer was also grafted with lactone monomers in a brush-like pattern. These brushes give the material its stretchability. The resulting 'Advanced Scalable Supersoft Elastic Transparent material' (ASSETm) has all the right properties. Experiments revealed that it is suited to seal in electrodes to produce sensors. 'We compared our sensors with stateof-the-art commercial sensors, and found that ours worked at least as well,' says Lan.

we do have to change our attitude towards starch, which is usually seen as a food product.' Currently, approximately 60% of all starch is used in animal feed, 30% for human consumption, and 10% in medical applications. 'However, starch consumption is decreasing, and there is a downward trend in cattle numbers.'

### Discussion

Group leader Katja Loos is also enthusiastic about the new material: 'We hope that our paper will launch a discussion on further curbing e-waste. This degradable polymer can really help reduce the amount of e-waste.'

Reference: Xiaohong Lan, Wenjian Li, Chongnan Ye, Laura Boetje, Théophile Pelras, Fitrilia Silvianti, Qi Chen, Yutao Pei, and Katja Loos: Scalable and Degradable Dextrin-Based Elastomers for Wearable Touch Sensing. ACS Applied Materials & Interfaces, 13 December 2022

The production process is scalable,

Zernike

### Quantum dots form ordered material Finding paves the way for new generation of opto-electronic applications

Quantum dots are clusters of some 1,000 atoms which act as one large 'superatom'. It is possible to accurately design the electronic properties of these dots just by changing their size. However, to create functional devices, a large number of dots have to be combined into a new material. During this process, the properties of the dots are often lost. Now, a team led by University of Groningen professor of Photophysics and Optoelectronics, Maria Antonietta Loi, has succeeded in making a highly conductive optoelectronic metamaterial through self-organization. The metamaterial is described in the journal Advanced Materials, published on 29 October.

Quantum dots of PbSe (lead selenide) or PbS (lead sulphide) can convert shortwave infrared light into an electrical current. This is a useful property for making detectors, or a switch for telecommunications, 'However, a single dot does not make a device. And when dots are combined, the assembly often loses the unique optical properties of individual dots, or, if they do maintain them, their capacity to transport charge carriers becomes very poor', explains Loi. 'This is because it is difficult to create an ordered material from the dots.'

#### **Ordered Layer**

Working with colleagues from the Zernike Institute for Advanced Materials at the Faculty of Science and Engineering, University of Groningen, Loi experimented with a method that allows the production of a metamaterial from



Colloidal quantum dots with truncated cube shape and their original ligands (organic molecules) assembling into an ordered superlattice after the ligand exchange. | Illustration Jacopo Pinna

a colloidal solution of quantum dots. These dots, each about five to six nanometres in size, show a very high conductivity when assembled in an ordered array, while maintaining their optical properties.

'We knew from the literature that dots can self-organize into a twodimensional, ordered layer. We wanted to expand this to a 3D material', says Loi. To achieve this, they filled small containers with a liquid that acted as a 'mattress' for the colloidal quantum dots. 'By injecting a small amount onto the surface of the liquid, we created a 2D material. Then, adding a bigger volume of quantum dots turned out to produce an ordered 3D material.'

### Superlattice

The dots are not submersed in the liquid, but self-orient on the surface to achieve a low energy state. 'The dots have a truncated cubic shape, and when they are put together, they form an ordered structure in three dimensions; a superlattice, where the dots act like atoms in a crystal', explains Loi. This superlattice that is composed by the quantum dot super atoms displays the highest electron mobility reported for quantum dot assemblies.



Electron microscope images showing two of the ordered structures formed in the experiments. Atoms inside the quantum dots are resolved by the microscope and it can be seen that they are aligned throughout adjacent dots. A model of the device used for the measurement of the electronic properties is shown in the bottom right. The superlattice lies between two electrodes while an ionic gel on top (gate electrode) is used to accumulate carriers in the active material. | Illustration Jacopo Pinna

#### Detectors

It took special equipment to ascertain what the new metamaterial looks like. The team used an electron microscope which has atomic resolution to show the details of the material. They also 'imaged' the large-scale structure of the material using a technique called Grazing-incidence small-angle X-ray scattering. 'Both techniques are available at the Zernike Institute, thanks to my colleagues Bart Kooi and Giuseppe Portale, respectively, which was a great help', says Loi.

Measurements of the electronic properties of the material show that it closely resembles that of a bulk semiconductor, but with the optical properties of the dots. Thus, the experiment paves the way to create new metamaterials based on quantum dots. The sensitivity of the dots used in the present study to infrared light could be used to create optical switches for telecommunication devices. 'And they might also be used in infrared detectors for night-vision and autonomous driving.'

#### ERC Grant

Loi is extremely pleased with the results of the experiments: 'People have been dreaming of achieving this since the 1980s. That is how long attempts have been made to assemble quantum dots into functional materials. The control of the structure and the properties we have achieved was beyond our wildest expectations.' Loi is now working on understanding and improving the technology to build extended superlattices from quantum dots, but is also planning to do so with other building blocks, for which she was recently awarded an Advanced Grant from the European Research Council. 'Our next step is to improve the technique in order to make the materials more perfect and fabricate photodetectors with them.'

Reference: Jacopo Pinna, K. Razieh Mehrabi, Dnyaneshwar S. Gavhane, Majid Ahmadi, Suhas Mutalik, Muhammad Zohaib, Loredana Protesescu, Bart J. Kooi, Giuseppe Portale and Maria Antonietta Loi: Approaching Bulk Mobility in PbSe Colloidal Quantum dots 3D Superlattices. Advanced Materials, 29 October 2022 Zernike

## Start-up Bioprex Medical makes medical implants safer

### By Renée Moezelaar

With an innovative new coating, researchers from the Zernike Institute for Advanced Materials and the UMCG have found a way to prevent bacterial infection on surgical implants and other medical devices. With their start-up Bioprex Medical, they hope to bring this coating to the market in the next few years.

Ton Loontjens, professor emeritus

When patients get implants, for instance a new knee or hip, doctors always have to be on the lookout for bacterial infection. No matter how clean they try to work, bacteria will always get through. One to five percent of the implant-patients will develop some kind of infection which can lead to the removal of the implant, serious illness or even death. With a new antibacterial coating, the new start-up Bioprex Medical wants to prevent these infections and make implant surgery saver.

### **Twenty Years**

Bioprex Medical was founded by

of material science at the Zernike Institute for Advanced Materials. "I have been working on these types of coatings for almost twenty years now", he says. "But eight years ago I got into contact with Pieter André de la Porte, director of Zorg Innovaties Nederland (Healhcare innovations in the Netherlands), and we started working on a commercial type of coating for medical applications." The coating Loontjens and his colleagues developed seemed to work well, so they decided to found a start-up: "Our coating has nice properties that suits medical applications, so we decided to take it one step further and try



Scanning electron microscopy image of S. Epidermidis on titanium (left image) or coated titanium (right image)

to bring it to the market."

The immobilized coating works on the basis of quaternary ammonium moieties that can kill bacteria when they come into contact. The main component is an unique hyperbranched polymer that the researchers developed themselves. "At the end of each branch we can add polyamines, that can be guaternized and turned into quaternary ammonium groups", Loontjens explains. "Because there are a lot of branches, there are a lot of these groups and this gives a high charge density. We found that such a high density attracts nearby bacteria and kills them on contact."

### Attached

The coating is covalently attached to the surface of the implant with a coupling agent, which gives a high strength and stability. Loontjens: "Another advantage is that the hyperbranched polymer is hydrophobic, so water can't reach the surface of the implant which prevents hydrolysis of the ADVANCED MATERIALS | SPRING 2023



Uncoated screws from Astrolabe Medical (top) and coated by BioPrex (bottom)

bonding to the surface of the implant." The whole process of applying the coating does need some more work. "Application of the initial academic coating used to take about eight days", Loontjens says. "We have reduced that to eight hours now, but our aim is to apply it even faster."

The start-up Bioprex Medical should help the researchers to make the leap towards the market. "We try to optimize the coating as far as we can", Loontjens says. "And meanwhile we are discussing our technology with companies that can apply coatings and companies that make medical implants." Even though there is still work to be done, Loontjens is optimistic about their chances: "All parties are very interested in bringing down the chances of infections during surgery, which is of course a very important goal that could actually save lives. So, we hope that in about three years we will have a first Bioprex-coated product on the market."

### Newsflash

Katja Loos elected President of the European Polymer Federation

Prof. Jasper Knoester Knight in the Order of the Netherlands Lion

### Antonija Grubišić-Čabo joins our team as assistant professor

Four FSE researchers, including Zernike Institute post-doc Adéla Melcrova, receive NWO XS grant

Molecular Biophysics PhD student Pedro Buzón receives Rubicon grant

KHMW "For Women in Science" honorable mention for Dr. Carmem Maia Gilardoni

ERC Advanced Grants for Maria Antonietta Loi and Bart van Wees

Dr. Georgian Nedelcu joins Zernike Office as Funding Officer

NWO XS grant for Andrea Giuntoli

Marcos Guimaraes receives 2D Materials: 2021 Outstanding Reviewer Award

Recent publication of the Faraji group selected as 2022 hot PCCP article

"Bert de Boer Poster Prize" for Chris van Ewijk

Open Competition Science-M grant for Rifka Vlijm

George Palasantzas receives funding from NWO Open Technology Programme

NWO XS grant for Wouter Roos

Rubicon grant for Carmem Maia Gilardoni

1st Zernike Institute PhD colloquium symposium

Bauer, Guimaraes, and van Wees partner in consortium receiving an NWO XL grant

Jennifer Hong wins poster prize at NWO CHAINS

Wouter Roos and Rifka Vlijm partner in consortium receiving an NWO XL grant

Moniek Tromp new scientific director of the Zernike Institute

Maria Antonietta Loi elected member of the European Academy of Sciences

Wouter Roos partner in EIC Pathfinder project

Maria Antonietta Loi and Jan Anton Koster partners in Horizon Europe consortia

ERC Starting Grant awarded to Marcos Guimaraes

Katja Loos wins NWO Team Science Award with HyBRit research group

Gilardoni wins the Ehrenfest-Afanassjewa thesis prize 2022



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